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(71)**Applicant**
Identification Number000002897
NameDai Nippon Printing Co., Ltd.
Address1-1-1, Ichigaya Kaga-cho, Shinjuku-ku, Tokyo
(72)**Inventor(s)**
Name**** Hidetoshi
Address1-1-1, Ichigaya Kaga-cho, Shinjuku-ku, Tokyo Inside of Dai Nippon Printing Co., Ltd.
(74)**Attorney**
Identification Number100077698
Patent Attorney
NameYoshida Katsuhiro (besides one person)
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(57) **Abstract**
Technical problem Even if you excel in the heat resistance of a liquid crystal / polymers bipolar membrane, etc. and also you repeat rewriting 100 times or more, provide the reversible display medium which is maintaining high printing contrast.
Means for SolutionA reversible display medium characterized by the above-mentioned polymers matrix being a polyisocyanate bridging body of thermosetting acrylics in a reversible display medium

with which a liquid crystal forms the liquid crystal / polymers bipolar membrane distributed in a polymers matrix on a conductive substrate.

Claim(s)

Claim 1A reversible display medium characterized by the above-mentioned polymers matrix being a polyisocyanate bridging body of thermosetting acrylics in a reversible display medium with which a liquid crystal forms the liquid crystal / polymers bipolar membrane distributed in a polymers matrix on a conductive substrate.

Claim 2 The reversible display medium according to claim 1 which thermosetting acrylics is a copolymer of acrylate (meta) and carries out 5-10-mol unit content of the monomeric unit which has an isocyanate group and a basis which has reactivity.

Claim 3 The reversible display medium according to claim 1 whose basis reacted to an isocyanate group is a hydroxyl group or a carboxyl group.

Claim 4 The reversible display medium according to claim 1 whose liquid crystal is a smectic liquid crystal.

Claim 5 The reversible display medium according to claim 1 with which a liquid crystal contains a dichroism pigment.

Claim 6 The reversible display medium according to claim 1 which has a protective layer on the surface of a liquid crystal / polymers bipolar membrane.

Detailed Description of the Invention

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Field of the Invention This invention has a response to an electric field or heat, and this reversible display medium can be broadly used as a rewritable card, a display, other reversible display media, etc. about the reversible display medium using the liquid crystal / polymers bipolar membrane which can perform a display and record of a variety of information.

0002

Description of the Prior Art Now, a liquid crystal is applied by various apparatus as a display material, and is put in practical use by a clock, a calculator, small television, etc. The thing of the display type called TN type or a STN type is adopted using a pneumatic liquid crystal as these liquid crystals. Although this kind of display device encloses a liquid crystal in the liquid crystal cell which has a transparent electrode and it comprises what provided the polarizing plate in both sides, Since the polarizing plate is used, an angle of visibility is narrow, the necessity of needing the back light of high power consumption, and making cell thickness uniform since luminosity is insufficient to large-area-izing is difficult, and, moreover, there are problems, like structure is complicated and a manufacturing cost is high.

0003 As a liquid crystal display medium which solves such a problem, the liquid crystal distributed element using the liquid crystal / polymers bipolar membrane which distributed the liquid crystal in the polymer matrix has been capturing the spotlight recently. Among these, even after the external energy for carrying out orientation of the liquid crystal is removed, since the oriented state of a liquid crystal is maintained, the thing using a smectic liquid crystal has memory nature, and is useful as a rewritable reversible display medium.

0004

Problem(s) to be Solved by the Invention In the rewritable reversible display medium using this smectic liquid crystal, although a liquid crystal / polymers bipolar membrane is formed on a conductive substrate and a protective layer is provided in a record display side if needed, In such a conventional reversible display medium, The heat resistance of a liquid crystal / polymers bipolar membrane and the mothball nature in a high temperature atmosphere are insufficient, The number of times of rewriting is also about 10 times, if rewriting exceeding 10 times is performed, a liquid crystal particle and matrix resin will dissolve with the heat applied at the time of printing, printing contrast falls, and there is a problem of applying to practicality.

0005 The heat resistance of the reversible display medium in which the conventional rewriting is possible is the heat resistance of the grade (SN transition point-30 **) of the liquid crystal to be

used, and was not able to be saved at a high temperature atmosphere for a long time. The example using fumarate system resin with a glass transition point high as matrix resin was known, and lamination where the adhesion over the substrate of a liquid crystal / polymers bipolar membrane is low, and sufficient in this case was also difficult. Therefore, even if the purpose of this invention is excellent in the heat resistance of a liquid crystal / polymers bipolar membrane, etc. and also repeats rewriting 100 times or more, there is in providing the reversible display medium which is maintaining high printing contrast.

0006

Means for Solving the Problem The above-mentioned purpose is attained by the following this inventions. That is, in a reversible display medium with which a liquid crystal forms the liquid crystal / polymers bipolar membrane distributed in a polymers matrix on a conductive substrate, this invention is a reversible display medium, wherein the above-mentioned polymers matrix is a polyisocyanate bridging body of thermosetting acrylics.

0007 By using an acrylic resin which constructed the bridge by polyisocyanate as a polymers matrix of a reversible display medium of a liquid crystal / polymers compound die, It excels in the heat resistance of a liquid crystal / polymers bipolar membrane, and a reversible display medium with which printing contrast does not fall even if it repeats 100 rewritings or more can be provided.

0008

Embodiment of the Invention Next, a desirable embodiment is mentioned and this invention is explained in more detail. As the reversible display medium of this invention shows drawing 1 the section schematically, on the substrate sheet, the conductive layer, and the liquid crystal / polymers bipolar membrane used as an electrode is laminated, and the protective layer is provided on it still more preferably. And as schematically shown in drawing 2, the particles of a liquid crystal are distributing independently the above-mentioned liquid crystal / polymers bipolar membrane in matrix resin.

0009 In this invention, it is characterized by using the polyisocyanate bridging body of thermosetting acrylics as a polymers matrix of the above-mentioned liquid crystal / polymers bipolar membrane. When the thermosetting acrylic resin used as matrix resin by this invention carries out copolymerization of the acrylate (meta), it is an acrylic copolymer obtained using the monomer of acrylic or others which has a basis which reacts to an isocyanate group in 5-10-mol% of total monomers (meta).

0010as for the heat-resistant improved effect of matrix resin, less than **5 mol %** is **the quantity of the above-mentioned reactive monomer** insufficient, and if the quantity of a reactive monomer exceeds 10-mol % on the other hand, since visibility when the liquid crystal currently distributed in a matrix crystallizes and it prints to an expression medium will fall, it is not desirable.

0011 In the above-mentioned copolymer, a hydroxyl group, an amino group, an epoxy group, a carboxyl group, etc. are mentioned as an isocyanate group and a basis which is reactivity, and a hydroxyl group and a carboxyl group are especially preferred from a reactant point with an isocyanate group. As an example of representation of the acrylic monomer which has such a hydroxyl group or a carboxyl group, 2-hydroxyethyl (meta) acrylate, acrylic acid, and methacrylic acid which are the resultants of acrylic acid (meta) and ethylene glycol are mentioned.

0012 As polyisocyanate over which the above-mentioned acrylic resin is made to construct a bridge, It is the polyisocyanate currently conventionally used for manufacture of polyurethane resin, the adhesives of a polyurethane system, etc., for example, those hydrogenation ghosts, such as tolylene diisocyanate, JIFUNIRU methane diisocyanate, xylylene diisocyanate, isophorone diisocyanate, and hexamethylene di-isocyanate, -- further -- being alike -- those dimers and a trimer are mentioned. Each of such polyisocyanates can be obtained from a commercial scene, and can be used by this invention. As for such polyisocyanates, it is preferred to add at a rate of two to 10 weight section per said acrylic resin 100 weight section.

0013 It is preferred to use the smectic liquid crystal excellent in especially memory nature as a liquid crystal used by this invention, although it is conventionally usable in any publicly known liquid crystal. As such a smectic liquid crystal, various kinds of smectic liquid crystals which can be obtained from Japan Energy are used, for example. Especially the contrast of a display image is high, and in order to obtain a reversible display medium with little a fall and disappearance of contrast also in low temperature or a high temperature region, it is preferred to use the liquid crystal of following general formula (I) - (VII).

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(R^1 shows the alkyl group or alkoxy group of the carbon numbers 8-18 among a formula.)

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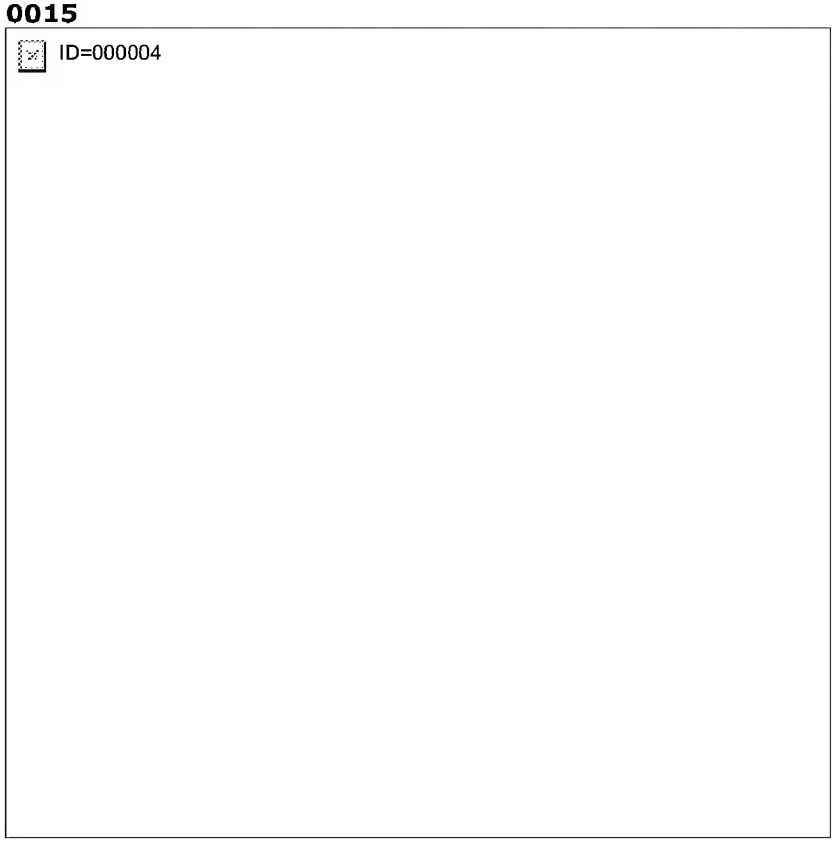

(R^2, R^3, R^4, R^5, R^6, and R^8 show the alkyl group of the carbon numbers 2-18 among a formula, R^7, R^9, and R^{10} show the alkyl group or alkoxy group of the carbon numbers 2-18, and X shows a halogen again.)

0016 The compound expressed with these general formula (II)s - (VII), The temperature rise of the phase transition temperature of a smectic liquid crystal phase-pneumatic liquid crystal phase or smectic liquid crystal phase-isotropic interphase is carried out, the record-keeping nature in an elevated temperature is so good that this phase transition temperature is high, and 60-130 ** is especially preferred not less than 60 **. It is good to choose suitably any one sort of the carbon numbers 2-18, or two sorts or more, to combine them, and to use them from each aforementioned compound kind of inside, so that this may be filled.

0017 As for the compound expressed with said general formula (II) - (VII), it is preferred to carry out 10-300 weight-section content to compound 100 weight section expressed with said general formula (I), and it is preferred to consider it as 20 to 240 weight section especially. 80:20-30:70, and thing 100 weight especially mixed by the ratio of 60:40-40:60 preferably are received by a weight section in the compound especially expressed with said general formula (I), and the compound expressed with general formula (II), If 5-100 weight-section content of one sort chosen from the compound expressed with general formula (IV) - (VII) or the two sorts or more is carried out preferably one to 200 weight section, Contrast is high, and especially since it becomes a liquid crystal composition which moreover does not have a fall or disappearance of contrast in a low temperature region as remarkable as not only an elevated temperature but -40 **, it is desirable.

0018 To these liquid crystal compositions, other liquid crystal compounds and additive agents can be added in the limit which does not destroy a smectic liquid crystal phase. It is suitable if a dichroism pigment is made to mix at a rate of one to 10 weight section per liquid crystal composition 100 weight section for the purpose of improvement, coloring, etc. of a contrast ratio especially for

example. By forming the liquid crystal / polymers bipolar membrane which distributed the liquid crystal composition in the polymer matrix using the aforementioned liquid crystal composition on a conductive substrate, the reversible display medium which can rewrite this invention is obtained. Although these desirable examples are shown concretely, this invention is not limited to this.

0019 As amount of the above-mentioned liquid crystal composition and said polymers matrix used, If the mixture ratio (weight ratio) of a polymers matrix / liquid crystal is 5 / 95 - 50/50 and there is too little amount of the liquid crystal used, In order to make a film into a transparent state for the transparency at the time of voltage one not only to to run short, but, it is insufficient in respect of needing great voltage etc., and if there is too much amount of the liquid crystal used on the other hand, since dispersion at the time of voltage OFF (turbidity) not only runs short, but membranous intensity will fall, it is not desirable.

0020 Although it is usable as a method of distributing a liquid crystal composition in a polymers matrix in each conventionally publicly known method, such as the phase separation method and an emulsion technique, in this invention, a useful method is the phase separation method. In the phase separation method, after preparing the solution which contains the above-mentioned ingredient using said polymers matrix and the above-mentioned liquid crystal composition, and the organic solvent that can dissolve other additive agents and applying this solution to a suitable substrates face, a solvent is evaporated and a liquid crystal / polymers bipolar membrane can be formed.

0021 As for the solids concentration of the solution which acetone, methyl ethyl ketone, toluene, xylene, a tetrahydrofuran, chloroform, etc. are mentioned, and consists of these solvents as a suitable solvent, for example, it is preferred to consider it as about 5 to 30% of the weight of the range. Stencil printing, brush coating, spray coating, braid coating, doctor coating, etc., for example, using screen-stencil and a metal mask as a method of forming a liquid crystal / polymers bipolar membrane on an electrode substrate are mentioned using the above solution.

0022 The electrode substrate (conductive substrate) used is conventionally generally used to a publicly known reversible display medium, and in this invention. It is usable and each conventionally publicly known conductive substrate is an electrode substrate of the couple which, concrete for example, made a transparent conductive material like ITO, a SnO_2 system, and a ZnO system adhere to transparent substrates, such as glass and a high polymer film. When using an opaque conductive substrate for other one side at this time, the substrate which that electrode formed for the aluminum reflector, for example since the function as a light reflector was also required is preferred. The substrate itself may be a thing of glass, a high polymer film, or others.

0023 After forming a liquid crystal / polymers bipolar membrane on an electrode substrate as mentioned above, the liquid crystal / polymers bipolar membrane which the polyisocyanate contained makes a reactant acrylic resin construct a bridge, and makes the purpose are formed by carrying out stoving at the temperature of the grade which does not affect a room temperature or a liquid crystal particle. In the above, since it is generally referred to as about 3-23 micrometers, the contrast of a display will become low if it is less than 3 micrometers, and driver voltage will become high if 23 micrometers is exceeded, the thickness of a liquid crystal / polymers bipolar membrane is not preferred.

0024 The reversible display medium which forms the liquid crystal / polymers bipolar membrane which liquid crystal composition particles distributed in the polymers matrix between the conductive substrates of a couple at least with transparent one side as one desirable embodiment of this invention is mentioned. The drive of this reversible display medium eliminates information by impression of voltage, and the writing of information is performed by impression of heat.

0025 The information displaying medium which formed the protective layer via the interlayer if needed on said liquid crystal / polymers bipolar membrane formed on the conductive substrate as other desirable embodiments is mentioned. A liquid crystal carries out orientation of the reversible display medium in which this kind of rewriting is possible by the voltage impressing from the protective layer side, light penetrates, information is eliminated, by heating, the orientation of a liquid crystal is in disorder and the writing of information is performed.

0026 The interlayer and thermosetting resin which consist of the same resin as the above-mentioned polymer matrix about an interlayer's formation, Ultraviolet curing nature resin or electron beam hardening resin, for example, polyene thiols, The polymerization nature acrylate polymer which has an acrylyl group (meta) in molecules, such as urethane acrylate, epoxy acrylate, and silicone acrylate. A reversible display medium rewritable by providing the protective layer which consists of publicly known hardening resin etc. which consist of monomers of monofunctional **, such as methyl**

methacrylate, or many organic functions can be formed.
0027 The card which can rewrite **of information** this embodiment is explained as an example. In the case of a card use, the electrode substrate to be used can be made into one sheet. Especially as a substrate of an electrode, a high polymer film is preferred. The white polyethylene terephthalate (PET) film as a film is desirable. The conductive layer can use metal other than transparent conductive materials, such as ITO, such as aluminum.
0028 In order to protect a liquid crystal / polymers bipolar membrane, it is preferred to provide a protective film on this bipolar membrane. Especially as a protective film, although not limited, the hardening resin which has a mechanical strength, a water resisting property, etc. is preferred. For example, UV or electron beam hardening type poly (meta) acrylate, polyurethane (meta) acrylate, etc. are used. When said protective layer film cannot be directly formed on a liquid crystal / polymers bipolar membrane, the thin film of water-soluble polymer, such as polyvinyl alcohol, may be made to form as an interlayer between this bipolar membrane and a protective film. the aforementioned protective coat material formed on another sheet -- transfer -- it laminates, and it may be made to harden and may form. In the case of a card use, in a display, the using rate of a liquid crystal and polymers differs in the fitness range, and the rate (weight ratio) of a liquid crystal/polymers has the preferred range of 55 / 45 - 35/65. In order to raise the contrast of a display, it is preferred to make a liquid crystal contain dichroic coloring matter.
0029 Next, record and elimination of the information on the card of the above-mentioned composition are explained. A required electric field is impressed and elimination of information is performed by making an electric field direction carry out orientation of the liquid crystal element, after heating a liquid crystal / polymers bipolar membrane layer. Especially as a method of impressing an electric field, a corona-electrical-charging method is effective. Record of information is performed by disturbing the orientation of the liquid crystal element of a portion which applied required heat to the bipolar membrane layer and to which heat was applied. As a method of applying heat, the method of using a thermal head is preferred.
0030
ExampleNext, an example and a comparative example are given and this invention is explained still more concretely. There is a weight reference the inside of a sentence "%."
** was mixed to what fully carried out the agitation mix of ingredient **of the example 1 following** ** - the **, and was dissolved, and the coating liquid a liquid crystal / for polymers bipolar membrane formation was prepared to it.
** a thermosetting acrylics solution (content 5MO RU% of 10% of solid content, and a hydroxyl group content monomer.) the Soken Chemical & Engineering make and a trade name M-1002 B-K6 120g** smectic liquid crystal (the Japan Energy make.) Trade name M-900054 8g** dichroism pigment (22 : 25:40 weight-ratio mixture of Japanese sensitizing dye company make and trade name G206:G241:G472) 0.16g** polyisocyanate (Japanese polyurethane company make, trade name coronate L)
0.64g**0031**After using and applying bar coating-machine #36 on an ITO vacuum evaporation white PET board and drying the coating liquid prepared above for 1 minute at 100 **, while putting in for 24 hours or more and making matrix resin construct a bridge into 60 ** oven, Phase separation of the liquid crystal was carried out to particles, and the liquid crystal / polymers bipolar membrane of 8 micrometers of thickness were formed. The doctor blade was used for ultraviolet curing nature resin (urethane acrylate) all over a liquid crystal / polymers bipolar membrane, and after spreading, ultraviolet rays were irradiated with and stiffened with the high-pressure mercury-vapor lamp (output/cm **of 120W** ^{2}), and it was considered as the reversible display medium of this invention as a protective layer of 2 micrometers of thickness.
0032 It replaced with thermosetting acrylics in comparative example 1 Example 1, the nonresponsive acrylic resin (the Soken Chemical & Engineering make, trade name M-1002B) was used, and others obtained the reversible display medium of the comparative example like Example 1. As for each reversible display medium of the above-mentioned example and the comparative example 1, the erasing state was acquired by corona discharge (corona voltage 6.5kv), and write states were acquired by the thermal recording by a thermal head etc.
0033 About the reversible display medium of the above-mentioned Example 1 and the comparative example 1, it prints by a thermal head by the printing condition of 0.8mJ/a dot, respectively, When printing was eliminated by corona discharge in the printing afterbaking state and this was repeated, printing contrast in which after 100 repetitions is sufficient in the case of the reversible display

medium of Example 1 was acquired, but as for the case of the comparative example 1, the contrast of printing fell remarkably by the repetition around 10 times. When the heat resistance of both reversible display media was investigated, also after neglecting the thing of Example 1 in 1-hour oven at 90 **, repetition rewriting was possible for it, but after neglecting the thing of a comparative example in 75 ** oven for 1 hour, printing contrast is falling remarkably.
It was impractical.

0034
Effect of the Invention By using like the above the acrylic resin which constructed the bridge by PORISO cyanate as a polymers matrix of the reversible display medium of a liquid crystal / polymers compound die according to this invention, It excels in the heat resistance of a liquid crystal / polymers bipolar membrane, and the reversible display medium with which printing contrast does not fall even if it repeats 100 rewritings or more can be provided.

Field of the Invention This invention has a response to an electric field or heat, and this reversible display medium can be broadly used as a rewritable card, a display, other reversible display media, etc. about the reversible display medium using the liquid crystal / polymers bipolar membrane which can perform a display and record of a variety of information.

Description of the Prior Art Now, a liquid crystal is applied by various apparatus as a display material, and is put in practical use by a clock, a calculator, small television, etc. The thing of the display type called TN type or a STN type is adopted using a pneumatic liquid crystal as these liquid crystals. Although this kind of display device encloses a liquid crystal in the liquid crystal cell which has a transparent electrode and it comprises what provided the polarizing plate in both sides, Since the polarizing plate is used, an angle of visibility is narrow, the necessity of needing the back light of high power consumption, and making cell thickness uniform since luminosity is insufficient to large-area-izing is difficult, and, moreover, there are problems, like structure is complicated and a manufacturing cost is high.
0003 As a liquid crystal display medium which solves such a problem, the liquid crystal distributed element using the liquid crystal / polymers bipolar membrane which distributed the liquid crystal in the polymer matrix has been capturing the spotlight recently. Among these, even after the external energy for carrying out orientation of the liquid crystal is removed, since the oriented state of a liquid crystal is maintained, the thing using a smectic liquid crystal has memory nature, and is useful as a rewritable reversible display medium.

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Means for Solving the Problem The above-mentioned purpose is attained by the following this inventions. That is, in a reversible display medium with which a liquid crystal forms the liquid crystal / polymers bipolar membrane distributed in a polymers matrix on a conductive substrate, this invention is a reversible display medium, wherein the above-mentioned polymers matrix is a polyisocyanate bridging body of thermosetting acrylics.

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0009 In this invention, it is characterized by using the polyisocyanate bridging body of thermosetting acrylics as a polymers matrix of the above-mentioned liquid crystal / polymers bipolar membrane. When the thermosetting acrylic resin used as matrix resin by this invention carries out copolymerization of the acrylate (meta), it is an acrylic copolymer obtained using the monomer of acrylic or others which has a basis which reacts to an isocyanate group in 5-10-mol% of total monomers (meta).

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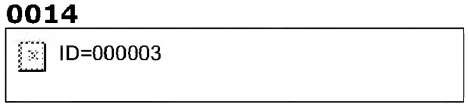

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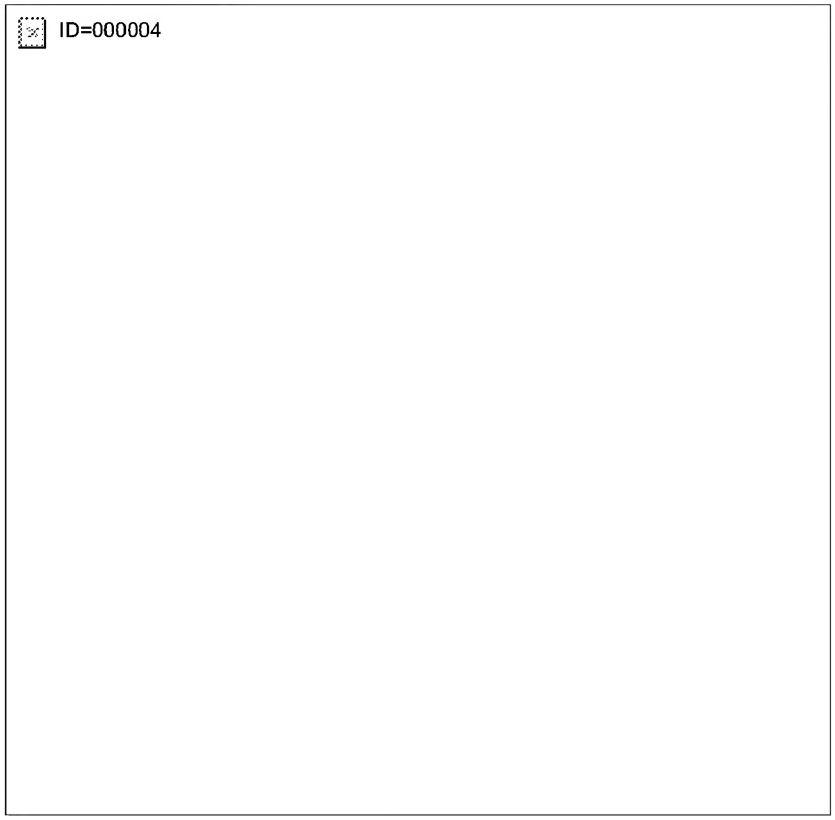


(R^2, R^3, R^4, R^5, R^6, and R^8 show the alkyl group of the carbon numbers 2-18 among a formula, R^7, R^9, and R^{10} show the alkyl group or alkoxy group of the carbon numbers 2-18, and X shows a halogen again.)

0016 The compound expressed with these general formula (II)s - (VII), The temperature rise of the phase transition temperature of a smectic liquid crystal phase-pneumatic liquid crystal phase or smectic liquid crystal phase-isotropic interphase is carried out, the record-keeping nature in an elevated temperature is so good that this phase transition temperature is high, and 60-130 ** is especially preferred not less than 60 **. It is good to choose suitably any one sort of the carbon numbers 2-18, or two sorts or more, to combine them, and to use them from each aforementioned compound kind of inside, so that this may be filled.

0017 As for the compound expressed with said general formula (II) - (VII), it is preferred to carry out 10-300 weight-section content to compound 100 weight section expressed with said general formula (I), and it is preferred to consider it as 20 to 240 weight section especially. 80:20-30:70, and thing 100 weight especially mixed by the ratio of 60:40-40:60 preferably are received by a weight section in the compound especially expressed with said general formula (I), and the compound expressed with general formula (II), If 5-100 weight-section content of one sort chosen from the compound expressed with general formula (IV) - (VII) or the two sorts or more is carried out preferably one to 200 weight section, Contrast is high, and especially since it becomes a liquid crystal composition which moreover does not have a fall or disappearance of contrast in a low temperature region as remarkable as not only an elevated temperature but -40 **, it is desirable.

0018 To these liquid crystal compositions, other liquid crystal compounds and additive agents can be added in the limit which does not destroy a smectic liquid crystal phase. It is suitable if a dichroism pigment is made to mix at a rate of one to 10 weight section per liquid crystal composition 100 weight section for the purpose of improvement, coloring, etc. of a contrast ratio especially for example. By forming the liquid crystal / polymers bipolar membrane which distributed the liquid crystal composition in the polymer matrix using the aforementioned liquid crystal composition on a conductive substrate, the reversible display medium which can rewrite this invention is obtained. Although these desirable examples are shown concretely, this invention is not limited to this.

0019 As amount of the above-mentioned liquid crystal composition and said polymers matrix used, If

the mixture ratio (weight ratio) of a polymers matrix / liquid crystal is 5 / 95 - 50/50 and there is too little amount of the liquid crystal used, In order to make a film into a transparent state for the transparency at the time of voltage one not only to to run short, but, it is insufficient in respect of needing great voltage etc., and if there is too much amount of the liquid crystal used on the other hand, since dispersion at the time of voltage OFF (turbidity) not only runs short, but membranous intensity will fall, it is not desirable.

0020 Although it is usable as a method of distributing a liquid crystal composition in a polymers matrix in each conventionally publicly known method, such as the phase separation method and an emulsion technique, in this invention, a useful method is the phase separation method. In the phase separation method, after preparing the solution which contains the above-mentioned ingredient using said polymers matrix and the above-mentioned liquid crystal composition, and the organic solvent that can dissolve other additive agents and applying this solution to a suitable substrates face, a solvent is evaporated and a liquid crystal / polymers bipolar membrane can be formed.

0021 As for the solids concentration of the solution which acetone, methyl ethyl ketone, toluene, xylene, a tetrahydrofuran, chloroform, etc. are mentioned, and consists of these solvents as a suitable solvent, for example, it is preferred to consider it as about 5 to 30% of the weight of the range. Stencil printing, brush coating, spray coating, braid coating, doctor coating, etc., for example, using screen-stencil and a metal mask as a method of forming a liquid crystal / polymers bipolar membrane on an electrode substrate are mentioned using the above solution.

0022 The electrode substrate (conductive substrate) used is conventionally generally used to a publicly known reversible display medium, and in this invention. It is usable and each conventionally publicly known conductive substrate is an electrode substrate of the couple which, concrete for example, made a transparent conductive material like ITO, a SnO_2 system, and a ZnO system adhere to transparent substrates, such as glass and a high polymer film. When using an opaque conductive substrate for other one side at this time, the substrate which that electrode formed for the aluminum reflector, for example since the function as a light reflector was also required is preferred. The substrate itself may be a thing of glass, a high polymer film, or others.

0023 After forming a liquid crystal / polymers bipolar membrane on an electrode substrate as mentioned above, the liquid crystal / polymers bipolar membrane which the polyisocyanate contained makes a reactant acrylic resin construct a bridge, and makes the purpose are formed by carrying out stoving at the temperature of the grade which does not affect a room temperature or a liquid crystal particle. In the above, since it is generally referred to as about 3-23 micrometers, the contrast of a display will become low if it is less than 3 micrometers, and driver voltage will become high if 23 micrometers is exceeded, the thickness of a liquid crystal / polymers bipolar membrane is not preferred.

0024 The reversible display medium which forms the liquid crystal / polymers bipolar membrane which liquid crystal composition particles distributed in the polymers matrix between the conductive substrates of a couple at least with transparent one side as one desirable embodiment of this invention is mentioned. The drive of this reversible display medium eliminates information by impression of voltage, and the writing of information is performed by impression of heat.

0025 The information displaying medium which formed the protective layer via the interlayer if needed on said liquid crystal / polymers bipolar membrane formed on the conductive substrate as other desirable embodiments is mentioned. A liquid crystal carries out orientation of the reversible display medium in which this kind of rewriting is possible by the voltage impressing from the protective layer side, light penetrates, information is eliminated, by heating, the orientation of a liquid crystal is in disorder and the writing of information is performed.

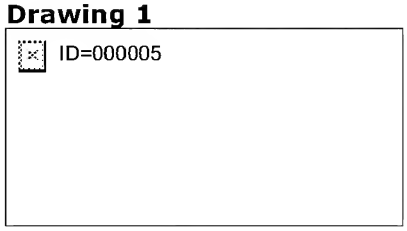
0026 The interlayer and thermosetting resin which consist of the same resin as the above-mentioned polymer matrix about an interlayer's formation, Ultraviolet curing nature resin or electron beam hardening resin, for example, polyene thiols, The polymerization nature acrylate polymer which has an acrylyl group (meta) in molecules, such as urethane acrylate, epoxy acrylate, and silicone acrylate. A reversible display medium rewritable by providing the protective layer which consists of publicly known hardening resin etc. which consist of monomers of monofunctional **, such as methyl methacrylate,** or many organic functions can be formed.

0027 The card which can rewrite **of information** this embodiment is explained as an example. In the case of a card use, the electrode substrate to be used can be made into one sheet. Especially as a substrate of an electrode, a high polymer film is preferred. The white polyethylene terephthalate (PET) film as a film is desirable. The conductive layer can use metal other than transparent

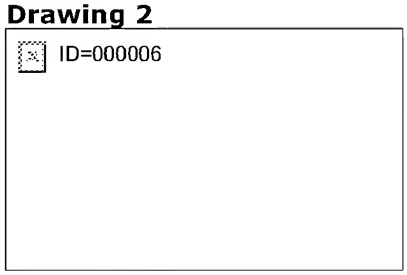
conductive materials, such as ITO, such as aluminum.
0028 In order to protect a liquid crystal / polymers bipolar membrane, it is preferred to provide a protective film on this bipolar membrane. Especially as a protective film, although not limited, the hardening resin which has a mechanical strength, a water resisting property, etc. is preferred. For example, UV or electron beam hardening type poly (meta) acrylate, polyurethane (meta) acrylate, etc. are used. When said protective layer film cannot be directly formed on a liquid crystal / polymers bipolar membrane, the thin film of water-soluble polymer, such as polyvinyl alcohol, may be made to form as an interlayer between this bipolar membrane and a protective film. the aforementioned protective coat material formed on another sheet -- transfer -- it laminates, and it may be made to harden and may form. In the case of a card use, in a display, the using rate of a liquid crystal and polymers differs in the fitness range, and the rate (weight ratio) of a liquid crystal/polymers has the preferred range of 55 / 45 - 35/65. In order to raise the contrast of a display, it is preferred to make a liquid crystal contain dichroic coloring matter.
0029 Next, record and elimination of the information on the card of the above-mentioned composition are explained. A required electric field is impressed and elimination of information is performed by making an electric field direction carry out orientation of the liquid crystal element, after heating a liquid crystal / polymers bipolar membrane layer. Especially as a method of impressing an electric field, a corona-electrical-charging method is effective. Record of information is performed by disturbing the orientation of the liquid crystal element of a portion which applied required heat to the bipolar membrane layer and to which heat was applied. As a method of applying heat, the method of using a thermal head is preferred.

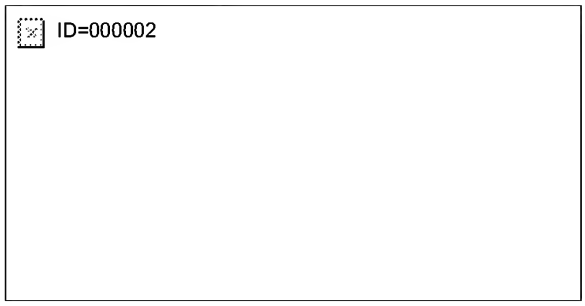
Brief Description of the Drawings
Drawing 1 The figure which illustrates the section of the reversible display medium of this invention schematically
Drawing 2 The figure which illustrates schematically the section of a liquid crystal / polymers bipolar membrane

Drawing 1



Drawing 2

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(71)出願人　000002897
大日本印刷株式会社
東京都新宿区市谷加賀町一丁目１番１号
(72)発明者　男澤　英敏
東京都新宿区市谷加賀町一丁目１番１号
大日本印刷株式会社内
(74)代理人　100077698
弁理士　吉田　勝広　（外１名）

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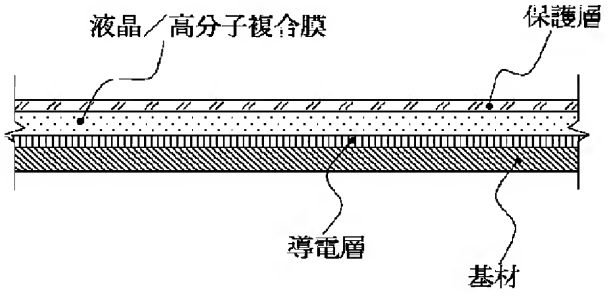
4H027 BA03 BB11 BD01 BE06

(54)【発明の名称】　可逆性表示媒体

(57)【要約】
【課題】　液晶／高分子複合膜の耐熱性等に優れ、更には書き換えを１００回以上繰り返しても高い印字コントラストを維持している可逆性表示媒体を提供すること。
【解決手段】　液晶が高分子マトリックス中に分散してなる液晶／高分子複合膜を導電性基板上に形成してなる可逆性表示媒体において、上記高分子マトリックスが熱硬化性アクリル樹脂のポリイソシアネート架橋体であることを特徴とする可逆性表示媒体。



【特許請求の範囲】
【請求項１】　液晶が高分子マトリックス中に分散してなる液晶／高分子複合膜を導電性基板上に形成してなる可逆性表示媒体において、上記高分子マトリックスが熱硬化性アクリル樹脂のポリイソシアネート架橋体であることを特徴とする可逆性表示媒体。
【請求項２】　熱硬化性アクリル樹脂が、（メタ）アクリレートの共重合体であって、イソシアネート基と反応性を有する基を有するモノマー単位を５～１０モル単位含有する請求項１に記載の可逆性表示媒体。
【請求項３】　イソシアネート基と反応する基が水酸基又はカルボキシル基である請求項１に記載の可逆性表示媒体。
【請求項４】　液晶がスメクチック液晶である請求項１に記載の可逆性表示媒体。
【請求項５】　液晶が二色性色素を含む請求項１に記載の可逆性表示媒体。
【請求項６】　液晶／高分子複合膜の表面に保護層を有する請求項１に記載の可逆性表示媒体。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、電界や熱に対して応答性を有し、各種情報の表示や記録を行うことができる液晶／高分子複合膜を用いた可逆性表示媒体に関し、かかる可逆性表示媒体は書き換え可能カード、ディスプレイ、その他の可逆性表示媒体等として幅広く使用することができる。
【０００２】
【従来の技術】現在、液晶は表示材料として種々の機器で応用され、時計、電卓、小型テレビ等に実用化されている。これらの液晶としてはネマティック液晶を用い、ＴＮ型或はＳＴＮ型と呼ばれる表示方式のものが採用されている。この種の表示素子は、透明電極を有する液晶セル中に液晶を封入し、両面に偏光板を設けたものから構成されているが、偏光板を用いているため、視野角が狭く、輝度が不足しているので、高消費電力のバックライトを必要とし、又、セル厚を均一にする必要から大面積化が困難であり、しかも構造が複雑で、製造コストが高い等の問題がある。
【０００３】このような問題を解決する液晶表示媒体として、最近、液晶を高分子マトリクス中に分散させた液晶／高分子複合膜を用いた液晶分散型素子が注目を浴びている。このうち、スメクチック液晶を利用するものは、液晶を配向させるための外部エネルギーが除去された後も、液晶の配向状態が維持されるためにメモリー性を持ち、書換可能な可逆性表示媒体として有用である。
【０００４】
【発明が解決しようとする課題】このスメクチック液晶を利用した書換可能な可逆性表示媒体には、液晶／高分子複合膜を導電性基板上に形成し、必要に応じて記録表示面に保護層が設けられたものであるが、従来のこのような可逆性表示媒体においては、液晶／高分子複合膜の耐熱性や高温雰囲気における長期保存性が不十分で、その書き換え回数も１０回程度であり、１０回を超える書き換えを行なうと印字時に加えられる熱によって液晶粒子とマトリックス樹脂とが相溶してしまい、印字コントラストが低下し、実用性にかけるという問題がある。
【０００５】又、従来の書換可能な可逆性表示媒体の耐熱性は、使用する液晶の（ＳＮ転移点－３０℃）程度の耐熱性であり、高温雰囲気に長時間保存することができなかった。又、マトリックス樹脂としてガラス転移点が高いフマレート系樹脂を用いる例も知られているが、この場合には液晶／高分子複合膜の基材に対する密着性が低く、又、十分な積層も困難であった。従って本発明の目的は、液晶／高分子複合膜の耐熱性等に優れ、更には書き換えを１００回以上繰り返しても高い印字コントラストを維持している可逆性表示媒体を提供することにある。
【０００６】
【課題を解決するための手段】上記目的は以下の本発明により達成される。即ち、本発明は、液晶が高分子マトリックス中に分散してなる液晶／高分子複合膜を導電性基板上に形成してなる可逆性表示媒体において、上記高分子マトリックスが熱硬化性アクリル樹脂のポリイソシアネート架橋体であることを特徴とする可逆性表示媒体である。
【０００７】液晶／高分子複合型の可逆性表示媒体の高分子マトリックスとして、ポリイソシアネートで架橋したアクリル樹脂を用いることによって、液晶／高分子複合膜の耐熱性に優れ、１００回以上の書き換えを繰り返しても印字コントラストが低下しない可逆性表示媒体を提供することができる。
【０００８】
【発明の実施の形態】次に好ましい実施の形態を挙げて本発明を更に詳しく説明する。本発明の可逆性表示媒体は図１にその断面を図解的に示すように、基材シートの上に電極となる導電層と液晶／高分子複合膜が積層され、更に好ましくはその上に保護層が設けられている。そして上記液晶／高分子複合膜は、図２に図解的に示すように、マトリックス樹脂中に液晶の粒子が独立して分散している。
【０００９】本発明では、上記液晶／高分子複合膜の高分子マトリックスとして熱硬化性アクリル樹脂のポリイソシアネート架橋体を使用したことを特徴としている。本発明でマトリックス樹脂として使用する熱硬化性のアクリル樹脂は、（メタ）アクリレートを共重合する際に、全モノマーの５～１０モル％をイソシアネート基と反応する基を有する（メタ）アクリル系又は他のモノマーを使用して得られるアクリル共重合体である。
【００１０】上記の反応性モノマーの量が５モル％未満

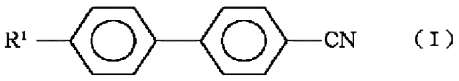
ではマトリックス樹脂の耐熱性向上効果が不十分であり、一方、反応性モノマーの量が１０モル％を超えると、マトリックス中に分散している液晶が結晶してしまい、表示媒体に印字した時の視認性が低下するので好ましくない。

【００１１】上記共重合体においてイソシアネート基と反応性である基としては、水酸基、アミノ基、エポキシ基、カルボキシル基等が挙げられ、特にイソシアネート基との反応性の点からは、水酸基及びカルボキシル基が好ましい。このような水酸基又はカルボキシル基を有するアクリルモノマーの代表例としては、（メタ）アクリル酸とエチレングリコールとの反応生成物である２－ヒドロキシエチル（メタ）アクリレート、アクリル酸、メタクリル酸が挙げられる。

【００１２】上記アクリル樹脂を架橋させるポリイソシアネートとしては、従来ポリウレタン樹脂の製造やポリウレタン系の接着剤等に使用されているポリイソシアネートであり、例えば、トリレンジイソシアネート、ジフニルメタンジイソシアネート、キシリレンジイソシアネート、イソホロンジイソシアネート、ヘキサメチレンジイソシアネート等、それらの水素添加化物、更ににはそれらの二量体、三量体が挙げられる。これらのポリイソシアネートはいずれも市場から入手して本発明で使用することができる。これらのポリイソシアネートは前記アクリル樹脂１００重量部当たり２～１０重量部の割合で添加することが好ましい。

【００１３】本発明で使用する液晶としては、従来公知のいずれの液晶でも使用可能であるが、特にメモリー性に優れたスメクチック液晶を使用することが好ましい。このようなスメクチック液晶としては、例えば、ジャパンエナジー社から入手できる各種のスメクチック液晶が使用される。特に表示画像のコントラストが高く、低温或は高温領域においてもコントラストの低下や消失が少ない可逆性表示媒体を得るには、下記一般式（Ｉ）～（VII）の液晶を使用することが好ましい。

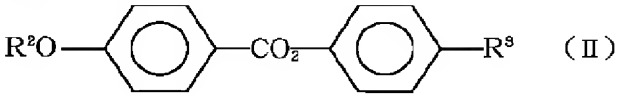
【００１４】



（Ⅰ）

（式中、R^1は炭素数８～１８のアルキル基又はアルコキシ基を示す。）

【００１５】



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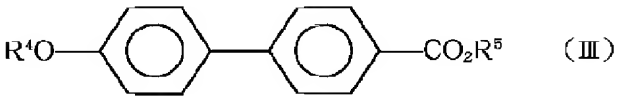

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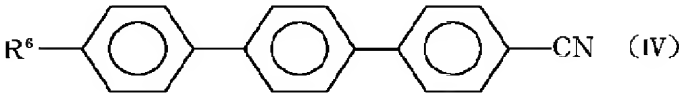

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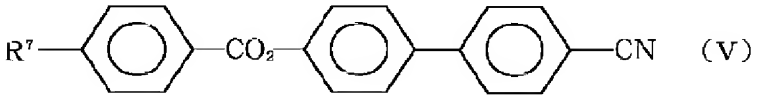

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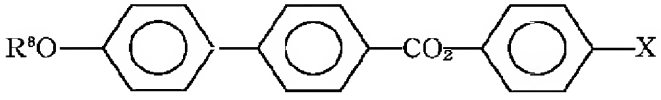

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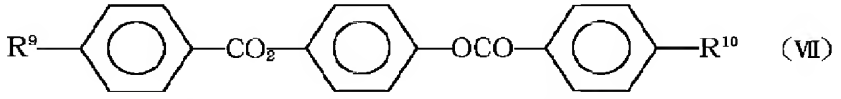


（Ⅶ）

（式中、R^2、R^3、R^4、R^5、R^6及びR^8は、炭素数２～１８のアルキル基を、R^7、R^9及びR^{10}は、炭素数２～１８のアルキル基又はアルコキシ基を、又、Ｘはハロゲン元素を示す。）

【００１６】これらの一般式（II）～（VII）で表される化合物は、スメクチック液晶相－ネマティック液晶相、或はスメクチック液晶相－アイソトロピック相間の相転移温度を高温化するものであり、この相転移温度が高いほど高温での記録保存性がよく、６０℃以上、特に６０～１３０℃が好ましい。これを満たすように前記の各々の化合物種の中から、炭素数２～１８のいずれか１種、或は２種以上を適宜選択して組み合わせて用いるとよい。

【００１７】前記一般式（II）～（VII）で表される化

合物は、前記一般式（Ｉ）で表される化合物１００重量部に対して１０～３００重量部含有させることが好ましく、特には２０～２４０重量部とすることが好ましい。又、特には、前記一般式（Ｉ）で表される化合物と一般式（II）で表される化合物とを、重量部で８０：２０～３０：７０、特に好ましくは６０：４０～４０：６０の比で混合したもの１００重量に対して、一般式（IV）～（VII）で表される化合物から選択される１種又は２種以上を１～２００重量部、好ましくは５～１００重量部含有させると、コントラストが高く、しかも高温のみならず、－４０℃というかなりな低温域においてもコントラストの低下や消失がない液晶組成物となるために特に好ましい。

【００１８】尚、これらの液晶組成物には、スメクチック液晶相を破壊しない限度において、他の液晶化合物や添加剤を添加することができる。特には、コントラスト比の向上や着色等を目的として、二色性色素を、例えば、液晶組成物１００重量部あたり１～１０重量部の割合で混入させると好適である。前記の液晶組成物を用いて高分子マトリクス中に液晶組成物を分散させた液晶／高分子複合膜を導電性基板上に形成することによって、本発明の書換可能な可逆性表示媒体が得られる。これらの好ましい例を具体的に示すが、本発明はこれに限定されるものではない。

【００１９】上記液晶組成物と前記高分子マトリックスの使用量としては、高分子マトリックス／液晶の混合比（重量比）が５／９５～５０／５０であり、液晶の使用量が少な過ぎると、電圧オン時の透明性が不足するだけでなく、膜を透明状態にするために多大の電圧を必要とする等の点で不十分であり、一方、液晶の使用量が多過ぎると、電圧オフ時の散乱（濁度）が不足するだけでなく、膜の強度が低下したりするので好ましくない。

【００２０】液晶組成物を高分子マトリックス中に分散する方法としては、相分離方法やエマルジョン法等の従来公知の方法がいずれも使用可能であるが、本発明において有用な方法は相分離方法である。相分離方法では、前記高分子マトリックス及び上記液晶組成物、その他の添加剤を溶解することができる有機溶剤を使用して上記成分を含む溶液を調製し、該溶液を適当な基板面に塗布した後、溶剤を蒸発させて液晶／高分子複合膜を形成することができる。

【００２１】好適な溶剤としては、例えば、アセトン、メチルエチルケトン、トルエン、キシレン、テトラヒドロフラン、クロロホルム等が挙げられ、これらの溶剤からなる溶液の固形分濃度は約５～３０重量％の範囲とすることが好ましい。以上の溶液を用いて、電極基板上に液晶／高分子複合膜を形成する方法としては、例えば、スクリーン印刷、メタルマスクを用いたステンシル印刷、刷毛塗り、スプレーコーティング、ブレードコーティング、ドクターコーティング等が挙げられる。

【００２２】使用される電極基板（導電性基板）は、従来公知の可逆性表示媒体に一般的に使用されているものであって、本発明では、従来公知の導電性基板はいずれも使用可能であり、具体的には、例えば、ＩＴＯ、SnO_2系、ＺｎＯ系のような透明導電性材料をガラスや高分子フイルム等のような透明基板に付着させた一対の電極基板である。この時、他の一方に不透明導電性基板を用いる場合には、その電極が反射板としての機能も要求されるため、例えば、アルミニウム反射電極を設けた基板が好ましい。その基板自体はガラス、高分子フイルム或いはその他のものであってもよい。

【００２３】上記のように電極基板上に液晶／高分子複合膜を形成した後、室温又は液晶粒子に影響を与えない程度の温度で加熱乾燥させることによって、含まれているポリイソシアネートが反応性アクリル樹脂を架橋させて目的とする液晶／高分子複合膜が形成される。上記においては、液晶／高分子複合膜の厚みは、一般的に３～２３μｍ程度とされ、３μｍ未満であると表示のコントラストが低くなり、又、２３μｍを越えると駆動電圧が高くなるので好ましくない。

【００２４】本発明の好ましい１実施態様として、液晶組成物粒子が高分子マトリックス中に分散した液晶／高分子複合膜を、少なくとも一方が透明である一対の導電性基板間に形成してなる可逆性表示媒体が挙げられる。この可逆性表示媒体の駆動は電圧の印加によって情報の消去を行い、熱の印加によって情報の書き込みが行われる。

【００２５】他の好ましい実施態様として導電性基板上に形成した前記液晶／高分子複合膜上に、必要に応じて中間層を介して保護層を形成した情報表示媒体が挙げられる。この種の書換可能な可逆性表示媒体は、保護層側からの電圧印加により液晶が配向して光が透過して情報が消去され、加熱によって液晶の配向が乱れて情報の書き込みが行われる。

【００２６】中間層の形成については、上記高分子マトリクスと同じような樹脂からなる中間層及び熱硬化性樹脂、紫外線硬化性樹脂或は電子線硬化樹脂、例えば、ポリエンーチオール類、ウレタンアクリレート、エポキシアクリレート、シリコーンアクリレート等の分子中に（メタ）アクリロイル基を有する重合性アクリレートポリマー類、メチルメタクリレート等の単官能又は多官能のモノマー類等からなる公知の硬化性樹脂等からなる保護層を設けることによって書換可能な可逆性表示媒体を形成することができる。

【００２７】この実施態様を情報の書き換え可能なカードを例として説明する。カード用途の場合、用いる電極基板は１枚とすることができる。電極の基板としては高分子フイルムが特に好適である。フイルムとしては白色のポリエチレンテレフタレート（ＰＥＴ）フイルムが望ましい。導電層はＩＴＯ等の透明導電性材料の他に、ア

ルミ等の金属を用いることができる。

【００２８】又、液晶／高分子複合膜を保護するために、該複合膜上に保護膜を設けることが好ましい。保護膜としては、特に限定されないが、機械的強度や耐水性等を有する硬化樹脂が好ましい。例えば、ＵＶ或は電子線硬化型のポリ（メタ）アクリレート、ポリウレタン（メタ）アクリレート等が用いられる。液晶／高分子複合膜上に直接前記保護層膜を形成することができない場合には、該複合膜と保護膜の間に、中間層としてポリビニルアルコール等の水溶性ポリマーの薄膜を形成させてもよい。又、別のシート上に形成した前記の保護膜材料を転写やラミネートして硬化させて形成してもよい。カード用途の場合、液晶と高分子の使用割合はディスプレイの場合とは適性範囲が異なり、液晶／高分子の割合（重量比）は５５／４５～３５／６５の範囲が好ましい。又、表示のコントラストを上げるために２色性の色素を液晶に含有させることが好ましい。

【００２９】次に、上記の構成のカードへの情報の記録及び消去について説明する。情報の消去は、液晶／高分子複合膜層を加熱した後、必要な電界を印加し、液晶分子を電界方向に配向させることによって行う。電界を印加する方法としては、コロナ帯電法が特に有効である。情報の記録は、複合膜層へ必要な熱を加え、熱が加えられた部分の液晶分子の配向を乱すことによって行う。熱を加える方法としては、サーマルヘッドを用いる方法が好ましい。

【００３０】

【実施例】次に実施例及び比較例を挙げて本発明を更に具体的に説明する。尚、文中「％」とあるのは重量基準である。

実施例１

下記の成分①～③を十分に混合撹拌して溶解したものに、④を混合して液晶／高分子複合膜形成用の塗布液を調製した。

① 熱硬化性アクリル樹脂溶液（固形分１０％、水酸基含有モノマーの含有量５モル％、綜研化学製、商品名Ｍ－１００２Ｂ－Ｋ６）　１２０ｇ

② スメクチック液晶（ジャパンエナジー社製、商品名M-900054）　８ｇ

③ 二色性色素（日本感光色素社製、商品名Ｇ２０６：Ｇ２４１：Ｇ４７２の２２：２５：４０重量比混合物）　０．１６ｇ

④ ポリイソシアネート（日本ポリウレタン社製、商品名コロネートＬ）　０．６４ｇ

【００３１】上記で調製した塗布液をＩＴＯ蒸着白ＰＥＴ基板上にバーコーター＃３６を用いて塗布し、１００℃で１分間乾燥させた後、６０℃のオーブン中に２４時間以上入れてマトリックス樹脂を架橋させるとともに、液晶を微粒子に相分離させ膜厚８μｍの液晶／高分子複合膜の成膜を行なった。更に、液晶／高分子複合膜の全面に紫外線硬化性樹脂（ウレタンアクリレート）をドクターブレードを用いて塗布後、高圧水銀灯（出力１２０Ｗ／ｃｍ²）で紫外線を照射して硬化させ膜厚２μｍの保護層として本発明の可逆性表示媒体とした。

【００３２】比較例１

実施例１における熱硬化性アクリル樹脂に代えて、非反応性のアクリル樹脂（綜研化学製、商品名Ｍ－１００２Ｂ）を使用し、他は実施例１と同様にして比較例の可逆性表示媒体を得た。上記実施例及び比較例１の可逆性表示媒体は、いずれもコロナ放電（コロナ電圧６．５ｋｖ）により消去状態が得られ、サーマルヘッド等による感熱記録によって書込状態が得られた。

【００３３】上記実施例１及び比較例１の可逆性表示媒体について、それぞれ０．８ｍＪ／ドットの印字条件でサーマルヘッドで印字し、印字後加熱状態でコロナ放電により印字の消去を行ない、これを繰り返したところ、実施例１の可逆性表示媒体の場合には１００回の繰り返し後も十分な印字コントラストが得られたが、比較例１の場合は１０回前後の繰り返しで印字のコントラストが著しく低下した。又、両方の可逆性表示媒体の耐熱性を調べたところ、実施例１のものは９０℃で１時間オーブン中に放置した後でも、繰り返し書き換え可能であったが、比較例のものは７５℃のオーブン中に１時間放置した後は、印字コントラストが著しく低下しており、実用性がなかった。

【００３４】

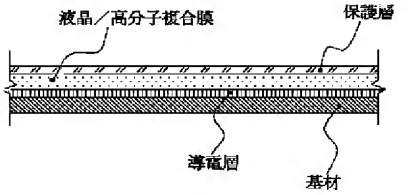
【発明の効果】以上の如く本発明によれば、液晶／高分子複合型の可逆性表示媒体の高分子マトリックスとして、ポリソシアネートで架橋したアクリル樹脂を用いることによって、液晶／高分子複合膜の耐熱性に優れ、１００回以上の書き換えを繰り返しても印字コントラストが低下しない可逆性表示媒体を提供することができる。

【図面の簡単な説明】

【図１】　本発明の可逆性表示媒体の断面を図解的に説明する図

【図２】　液晶／高分子複合膜の断面を図解的に説明する図

【図１】



【図２】